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The Role of Solvent Reorganization Dynamics in Electron-Transfer Processes. Theory-Experiment Comparisons
For Electrochemical and Homogeneous Electron Exchange
Involving Metallocene Redox Couples

by

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Abstract

Electrochemical Rate Constants and Activation Parameters are reported for the electron exchange of five metallocene couples and dibenzenechromium(I)/(0) in eight solvents at mercury electrodes. The solvents (acetonitrile, acetone, methylene chloride, formamide, N-methylformamide, N,N'-dimethylformamide, dimethylsulfoxide, and benzonitrile) were chosen so to provide substantial variations in their dynamical as well as dielectric properties. The metallocene couples are of the form $M(Cp)_2^{(+)}$, where M = Fe, Co, or Mn, and Cp = cyclopentadiene or pentamethylcyclopentadiene. The inner-shell (i.e., bond distortional) barriers are calculated for the metallocene and arene couples from bond-distance and vibrational data to be small (~ 0.25 kcal/mol) yet metal-dependent. Detailed comparisons of the observed solvent-dependent kinetics are made with the rate parameters calculated from contemporary theoretical treatments of outer-sphere electron transfer. Considerably better agreement between the experimental and theoretical kinetic parameters was obtained when the latter take into account the influence of solvent friction upon the barrier-crossing frequency. A comparison between the corresponding experimental and theoretical rate parameters for ferricinium-ferrocene self exchange in eight solvents yielded a similar finding. These results indicate that the conventional transition-state theory may not apply to electron-transfer reactions where the free-energy barrier is due chiefly to solvent reorganization, at least in "high friction" media where concerted solvent relaxation is slow. The likely influences of the solvent upon the kinetics of other outer-sphere reactions is also discussed in the light of these findings.

A particularly interesting class of condensed-phase reactions is provided by electron exchange involving redox couples with little or no molecular structural changes, since the kinetics will be determined largely by solvent reorganization. Detailed examination of such processes as a function of solvent properties can therefore provide direct tests of the solvent reorganization energetics as described by contemporary theoretical models.^{1,2} An intriguing recent development concerns the emergence of detailed theoretical treatments of solvent reorganization dynamics in condensed-phase reactions,² including electron transfer.^{2a-e} These models predict that the dynamical, as well as dielectric, solvent properties can exert a dominant influence upon the barrier-crossing rates.²

Experimental work has focussed attention on electron exchange of aromatic molecule-radical anion redox couples in homogeneous aprotic media³ and at electrochemical interfaces,⁴ although few studies have been concerned with detailed solvent effects. Another class of such reactions involves organometallic complexes, especially those containing aromatic groups such as cyclopentadienyl and arene ligands. A number of these complexes exhibit reversible one-electron reduction or oxidation in a wide variety of solvents, with only minor changes in metal-ligand bond lengths attending electron transfer so that the inner-shell activation energies are small ($\leq 0.3 \text{ kcal mol}^{-1}$), yet variable. In addition, these reactions commonly involve either uncharged or singly charged reactants and products, thereby minimising the influence of electrostatic work terms on the measured kinetics. Nevertheless, surprisingly few studies of their electron-transfer kinetics have been undertaken.⁵

In the present paper, we report standard electrochemical rate constants and activation parameters extracted from a.c. impedance measurements for ferricinium-ferrocene, manganicinium-manganocene, cobalticinium-cobaltocene, and

dibenzo-chromium(I)/(0) couples, at a mercury electrode in dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), formamide, acetonitrile, acetone, methylene chloride (CH_2Cl_2), and benzonitrile. A preliminary account is also available.⁶ These solvents were selected on the basis of their well-defined electrochemical behavior, and to provide a variety of dielectric and dynamical environments (*vide infra*). Although standard rate constants for ferricinium-ferrocene in nonaqueous media have been reported recently by several workers,⁷ these values were obtained at solid surfaces using techniques under conditions where the quantitative validity of the derived rates is questionable.⁸

A major factor leading us to select such couples for detailed study is the availability of solvent-dependent rate parameters for homogeneous self exchange of ferricinium-ferrocene $[\text{Fe}(\text{Cp})_2]^{+/\circ}$, Cp = cyclopentadiene] and for several methyl derivatives.⁴ Although the formal potential for ferricinium-ferrocene itself is inconveniently close to the anodic limit in most solvents at mercury, the decamethyl derivative $[\text{Fe}(\text{Cp}')_2]^{+/\circ}$, where Cp' = pentamethylcyclopentadiene] exhibits formal potentials that are close to the potentials of zero charge, thereby minimising work-term ("double layer") effects. Besides the latter couple, electrochemical rate parameters were obtained in each solvent for $\text{Mn}(\text{Cp}')_2^{+/\circ}$, $\text{Co}(\text{Cp}')_2^{+/\circ}$, $\text{Co}(\text{Cp})_2^{+/\circ}$ and $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/\circ}$. All of these couples have small or negligible inner-shell barriers as derived from known structural parameters; they nevertheless exhibit widely different formal potentials that enable the possible influence of the double layer on the rate parameters to readily be assessed.

The present study constitutes the first systematic evaluation of electrochemical reactivities for metallocene and arene species. The comparisons presented herein with corresponding homogeneous reactivities and with rate

parameters obtained from contemporary theory demonstrate the significance of solvent reorganization dynamics to such simple outer-sphere processes in both heterogeneous and homogeneous reaction environments.

EXPERIMENTAL SECTION

Acetonitrile and methylene chloride (Burdick and Jackson) were dried with calcium hydride, subjected to three freeze-pump-thaw cycles, and normally vacuum distilled before use. DMF, NMF, formamide, DMSO, benzonitrile and acetone (Burdick and Jackson) were degassed and stored in an inert atmosphere dry box.

The tetrabutylammonium hexafluorophosphate (TBAHP) supporting electrolyte was prepared from ammonium hexafluorophosphate (Ozark Mahoning Co.) and tetrabutylammonium bromide (Eastman Kodak) by crystallization from acetone; it was recrystallized twice from ethanol and dried in a vacuum oven. Tetraethylammonium perchlorate (TEAP) (G. F. Smith) was recrystallized thrice from water and dried in a vacuum oven. All solutions were prepared in a dry box under nitrogen. Ferrocene, decamethylferrocene, and cobalticinium hexafluorophosphate were obtained from Strem Chemicals. Decamethylmanganocene was prepared as in ref. 9a, decamethylcobalticinium hexafluorophosphate as in ref. 9b, and dibenzenechromium as in ref. 5c.

The observed "standard" rate constants for electrochemical exchange k_{ob} , along with the corresponding transfer coefficients, α_{ob} , were determined at a dropping mercury electrode (mechanically controlled drop time 2 sec, flow rate ca. 2 mg sec^{-1}), by using a.c. polarography as described in refs. 8a and 10. This employed a PAR 173/179 potentiostat, a PAR 175 potential programmer, and a PAR 5204 lock-in amplifier. Frequencies between 100-1400 Hz were employed; the in-phase and quadrature current components were acquired and analyzed using

a LSI 11-23 microcomputer system. Values of k_{ob} were obtained from the dependence of the ratio of in-phase to quadrature currents as a function of frequency in the conventional manner. The a.c. polarographic data were corrected both for the effects of uncompensated solution resistance (R_{us}) as well as for distortions of the time-dependent readout of the lock-in amplifier caused by the necessary use of the low-pass filter.¹¹ Although positive-feedback iR compensation was employed, the former effect can be significant for k_{ob} values approaching the measurement limit since small positive values of R_{us} will inevitably remain. We have recently discussed this matter elsewhere.^{8a} Both the above corrections were applied most conveniently with the aid of digitally simulated polarograms using known distorting parameters (R_{us} , double-layer capacitance, amplifier time constant) for a series of trial values of k_{ob} in order to obtain the best fit with the observed polarographic response.^{8a} Application of these corrections generally acted to increase the derived k_{ob} values, although usually by factors of 50% or less provided that small lock-in amplifier time constants (< 0.03 sec) were employed. The k_{ob} values reported here are somewhat (ca. 2 fold) higher than those reported in a preliminary communication;⁶ the latter were obtained without application of the above corrections and using a longer amplifier time constant (0.15 sec).

Either the oxidized or reduced forms of the redox couple were present in solution (ca. 0.5 - 2 mM), depending on synthetic convenience. Almost all reactions displayed chemical reversibility on the cyclic voltammetric time-scale (50-500 mV sec⁻¹), as evidenced from equality of the cathodic and anodic peak currents. The exception is the electrooxidation of $Mn(Cp')$ ₂, which yielded significantly smaller reverse (cathodic) currents in the most strongly coordinating solvents (DMF, DMSO) at slower scan rates (< 0.5 V sec⁻¹). Nevertheless, satisfactory a.c. polarograms were obtained for each of these systems.

Temperature control ($\pm 0.1^\circ\text{C}$) was achieved by means of a jacketed cell through which water was circulated from a Braun Melsungen thermostat. All electrode potentials were measured versus an aqueous saturated calomel electrode (s.c.e.) using a cell containing a pair of "fine grade" glass frits so to avoid any contamination of the nonaqueous solution.

RESULTS AND THEORETICAL ANALYSES

Rate Constants

Tables I and II contain thermodynamic, structural, and other pertinent parameters for the redox couples and solvents studied in the present work. Values of the formal potential, E_f , at 23°C and the reaction entropy, ΔS_{rc}^* , are given for each redox couple in Table I. The latter were obtained from the temperature derivative of E_f using a nonisothermal cell arrangement.¹² (Although only representative values of E_f and ΔS_{rc}^* are given for most couples due to space limitations, the omitted values can readily be estimated since the solvent dependence of E_f and ΔS_{rc}^* are virtually the same for each couple.) Table III contains a summary of the observed rate constants for electrochemical exchange, k_{ob} (cm sec^{-1}), for each redox couple in the eight solvents studied here. (The gaps in this compilation arise from difficulties in obtaining suitably reliable values of k_{ob} due to spurious a.c. polarographic behavior associated with adsorption, insolubility, solvent background currents, etc.) The observed transfer coefficients, α_{ob} , were determined to be uniformly close to 0.50 (± 0.03). The rate constants were reproducible typically to $\pm 20\%$. We also anticipate a similar level of accuracy, except for the largest k_{ob} values (ca. $2-4 \text{ cm sec}^{-1}$; *vide supra*), since these are close to the maximum rate constants that can be evaluated using our instrumentation.^{8a,10}

The rate parameters in Table III were obtained using 0.1 M TBAHP as the supporting electrolyte. It is expected that k_{ob} will differ from the

"double-layer corrected" standard rate constants, k_{corr} , that would be obtained in the absence of the diffuse-layer potential, ϕ_d , by²⁹

$$\ln k_{corr} = \ln k_{ob} + (Z - \alpha_{corr}) \phi_d F/RT \quad (1)$$

where Z is the charge number of the oxidized species and α_{corr} is the cathodic work-corrected transfer coefficient, [$= -(RT/F)d\ln k_{corr}/dE$]. Application of Eq. (1) to the present systems by estimating ϕ_d from electrode charge-potential data using the Gouy-Chapman model³⁰ leads to the prediction that k_{corr} should be as much as 5-8 fold smaller than k_{ob} , depending on the redox couple. However, several lines of evidence indicate that $k_{ob} \approx k_{corr}$ (at least within ca. 50%), so that the magnitude of the double-layer corrections are markedly smaller than predicted by Eq. (1). Thus k_{ob} is virtually independent of the supporting electrolyte concentration, as well as the nature of the cation, over the range 0.05 to 0.5 M. In contrast, ionic strength-dependent values of k_{ob} , the variations being roughly in accordance with Eq. (1), are obtained under these conditions for several structurally related anionic redox couples. Further details are given in ref. 31.

The surprisingly small extent of the double-layer corrections for the present systems may be due to the preferential approach of the partially negatively charged cyclopentadiene rings to the electrode surface compensating the effect of the net positive charge of the complex upon the work terms that is anticipated from Eq. (1).^{31,32} We have also obtained closely similar (within ca. twofold) values of k_{ob} for the present metallocene couples at platinum electrodes using a.c. voltammetry.^{8b} All these k_{ob} values are markedly larger than some values reported previously;^{7a,c} we suspect that the latter suffer from systematic errors associated with solution resistance effects.^{8a}

The major thrust of this work is to compare these solvent-dependent rate parameters with the corresponding quantities obtained from theoretical descriptions

of solvent reorganization. We can express the work-corrected rate constant of an exchange reaction either in homogeneous solution or at an electrode surface as¹

$$k_{\text{corr}} = A \exp[-(\Delta G_{\text{os}}^* + \Delta G_{\text{is}}^*)/RT] \quad (2)$$

where A is a preexponential factor, and ΔG_{os}^* and ΔG_{is}^* are the components of the intrinsic free-energy barrier associated with outer-shell (solvent) and inner-shell (metal-ligand, etc.) reorganization, respectively. Calculated rate constants, k_{cal} , were obtained for comparison with the experimental values, k_{ob} , as follows.

Estimates of ΔG_{is}^* were determined from³³

$$\Delta G_{\text{is}}^* = 0.5 \sum f_{\text{is}} [(\Delta a)/2]^2 \quad (3)$$

where Δa is the change in a given bond distance between the oxidized and reduced forms of the redox couple, and f_{is} is the force constant of this bond. The latter is obtained from

$$f_{\text{is}} = 4\pi^2 v_{\text{is}}^2 \mu \quad (4)$$

where v_{is} is the observed frequency (sec^{-1}), and μ is the reduced mass of the vibrating bond. For the present redox couples the only significant structural change is the increase (or decrease) of the metal-ring distance. Fortunately, accurate X-ray structural data are available for both oxidized and reduced forms of most reactants studied here so that satisfactory estimates of Δa can be obtained.¹³⁻¹⁶ These are listed in Table I along with the literature sources. The corresponding values of v_{is} are also given in Table I, obtained or estimated from Raman spectroscopic data as described in the footnotes. They refer to the symmetrical stretch of both rings with respect to the metal center, so that μ is set equal to the ligand mass. The resulting estimates of ΔG_{is}^* obtained from Eqs. (3) and (5) (Table I) are all small ($\leq 0.25 \text{ kcal mol}^{-1}$), especially

for $Mn(Cp')_2^{+/\circ}$ ($\Delta G_{is}^* = 0.025 \text{ kcal mol}^{-1}$). (Note that an inner-shell barrier of $0.25 \text{ kcal mol}^{-1}$ will act to decrease k_{ob} by only 50%.)

The outer-shell reorganization energies were calculated from³⁴

$$\Delta G_{os}^* = \frac{e^2}{8} \left(\frac{1}{a} - \frac{1}{R_e} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (5)$$

where e is the electronic charge, a is the reactant radius, R_e is twice the reactant-electrode distance, and ϵ_{op} and ϵ_s are the optical and static dielectric constants, respectively, for the surrounding solvent. The resulting estimates of ΔG_{os}^* for each solvent are given in Table II; they were obtained from the literature values of ϵ_{op} and ϵ_s also listed in Table II, by assuming that $a = 3.8 \text{ \AA}$,³⁵ and $R_e = \infty$. The last assumption is tantamount to neglecting the reactant-electrode imaging interactions in the transition state³⁷ (*vide infra*).

In order to obtain calculated rate constants it remains to estimate the preexponential factor A in Eq. (2). For electrochemical as well as homogeneous reactions it is useful to consider that activation occurs within a previously formed "precursor complex" with the reactant pair (or the reactant-electrode pair) in suitably close proximity.^{5b,38-40} One can then write³⁸

$$A = K_p \kappa_{el} v_n \quad (6)$$

where K_p is an equilibrium constant for forming the precursor state, κ_{el} is the electronic transmission coefficient and v_n (sec^{-1}) is the nuclear frequency factor. The effective value of $K_p \kappa_{el}$ will be sensitive to the dependence of κ_{el} upon the reactant-electrode separation.^{38,41} Nevertheless, a provisional estimate of $K_p \kappa_{el}$, ca. $6 \times 10^{-9} \text{ cm}$, is obtained for electrochemical reactions by assuming that κ_{el} approaches unity (i.e., adiabaticity is achieved) only at the plane of closest approach.^{41,42}

The values of v_n are of central interest here. This quantity can be determined both by bond vibrations and solvent reorientation, associated with the characteristic frequencies v_{is} and v_{os} , respectively, since these motions comprise the free-energy barrier. A simple formula⁴³ which has been employed recently^{1d} is

$$v_n = \left(\frac{v_{os}^2 \Delta G_{os}^* + v_{is}^2 \Delta G_{is}^*}{\Delta G_{os}^* + \Delta G_{is}^*} \right)^{1/2} \quad (7)$$

Even though $\Delta G_{os}^* \gtrsim 20 \Delta G_{is}^*$ for the present reactions (Tables I, II), according to Eq. (7) v_{is} may still provide the predominant contribution to v_n if $v_{os} \ll v_{is}$. Anticipating this possibility (*vide infra*), inserting the typical values $\Delta G_{is}^* = 0.2 \text{ kcal mol}^{-1}$, $v_{is} = 6 \times 10^{12} \text{ sec}^{-1}$ along with ΔG_{os}^* (Table II) into Eq. (7) yields $v_n \sim 1.2 (\pm 0.1) \times 10^{12} \text{ sec}^{-1}$, essentially independent of the solvent. Inserting this along with $K_{p,el} \times 10^{-9} \text{ cm}$ into Eq. (6) yields $A = 7 \times 10^3 \text{ cm sec}^{-1}$. This together with the estimates of ΔG_{is}^* and ΔG_{os}^* (Tables I, II) inserted into Eq. (2) yields the calculated rate constants denoted " k_{cal} (Eq. 7)", listed in Table III. Comparison between the corresponding values of k_{cal} (Eq. 7) and k_{ob} (Table III) shows that although the calculated and observed rate constants are generally within ca. 20-fold, the solvent dependence of k_{cal} is in sharp qualitative disagreement with experiment.

Recent theoretical treatments of solvent reorganization dynamics have emphasised that the effective value of v_{os} can be related closely to the longitudinal (or "constant charge") solvent relaxation time, τ_L .² This quantity can be extracted from the Debye relaxation time, τ_D , determined from dielectric loss measurements using⁴⁴

$$\tau_L = (\epsilon_\infty / \epsilon_s) \tau_D \quad (8)$$

where ϵ_∞ is the high-frequency dielectric constant.⁴⁵ For relatively "high friction" solvents, say for $\tau_L \gtrsim 10^{-12}$ sec, the effective outer-shell frequency factor can be expressed for exchange reactions as^{2,47}

$$\nu_{os} = \tau_L^{-1} \left(\frac{\Delta G^*}{4\pi k_B T} \right)^{1/2} \quad (9)$$

where k_B is the Boltzmann constant. Such relations have not been applied previously to outer-sphere reactions. Nevertheless, a recent study of activation-less electron transfer within an extended aromatic system in a series of alcohol solvents indicates that the rates correlate with the solvent relaxation times,⁴⁸ and a connection between τ_L^{-1} and the solvent dependence of k_{ob} for some electrochemical reactions has been established empirically.⁴⁹

It is important to note that while Eq. (7) is based on the presumption that the transition-state theory (TST) applies, Eq. (9) describes deviations from TST caused by sluggish solvent relaxation. Physically, this corresponds to the system being obliged to recross the transition region many times for reaction to occur since the required concerted motion of the surrounding solvent molecules is strongly impeded. Calef and Wolynes^{2a} refer to this circumstance as "overdamped" solvent reorientation. They also point out that when this relaxation is relatively fast ($\tau_L \lesssim 10^{-12}$ sec), the effective value of ν_{os} may be limited by "solvent inertial" effects.^{2a} Since this "underdamped" relaxation rate refers to the smooth unimpeded crossing of the system over the transition state, it corresponds to the onset of the TST limit. A simple formula for ν_{os} under these conditions is^{2a,50}

$$\nu_{os} = (2\pi\tau_{rot})^{-1} (2\epsilon_s \gamma)^{1/2} \quad (10)$$

where τ_{rot} is the solvent rotational relaxation time, estimated from the moment of inertia of the solvent molecules, I, using

$$\tau_{\text{rot}} = (I/k_B T)^{1/2} \quad (10a)$$

Also,

$$\gamma = \frac{4\pi}{3} \frac{\rho \mu^2}{k_B T} \frac{1}{(\epsilon_s - 1)} \quad (10b)$$

where ρ is the molar density of the solvent and μ is its effective dipole moment.

The effective value of v_{os} when both τ_L and τ_{rot} contribute significantly is^{2a}

$$v_{os} = (2\pi c \tau_L)^{-1} [0.5 + 0.5(1 + \frac{2}{c \epsilon_0 \gamma} \frac{\tau_{\text{rot}}^2}{\tau_L^2})^{1/2}]^{-1} \quad (11)$$

where $c = (k_B T / \pi \Delta G_{os}^*)^{1/2}$. Although this definition of c only applies to "weakly adiabatic" electron transfer (where the electronic matrix coupling element $H_{12} \leq k_B T$), this condition is probably met for most outer-sphere, including electrochemical, reactions.^{41,51,52}

Values of v_{os} estimated from Eq. (9) and (11) are listed for each solvent in Table II. Note that for solvents where $\tau_L > 1 \times 10^{12} \text{ sec}^{-1}$, v_{os} (Eq 9) $\approx v_{os}$ (Eq 11); otherwise v_{os} (Eq 9) $> v_{os}$ (Eq 11). Rather than inserting these estimates of v_{os} into the TST expression Eq. (7), we provisionally set $v_{os} = v_n$ (vide infra). Combining them with the values of ΔG_{is}^* , ΔG_{os}^* , and $K_{p,el}^*$ noted above into Eqs. (2) and (6), yields the calculated rate constants, k_{cal} (Eq 9) and k_{cal} (Eq 11), respectively, that are also listed in Table III. In contrast to k_{cal} (Eq 7), these latter rate constants vary with the solvent roughly in accordance with the experimental values, k_{ob} , for all five redox couples. Moreover, the values of k_{cal} (Eq 9) are within at least 2-3 fold of k_{ob} in each solvent.

Activation Parameters

In order to obtain further insight into the factors influencing k_{ob} and to provide a more stringent test of the theoretical models, it is desirable to evaluate activation parameters in addition to rate constants at a single temperature. Although electrochemical activation parameters are seldom evaluated, we have repeatedly emphasised their usefulness.^{19,53} Table IV lists electrochemical activation parameters for three redox couples, $\text{Fe}(\text{Cp}')_2^{+/\circ}$, $\text{Co}(\text{Cp})_2^{+/\circ}$ and $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/\circ}$, measured in each solvent. The observed activation enthalpies, ΔH_{ob}^* (kcal mol^{-1}), were obtained from the temperature dependence of k_{ob} using

$$\Delta E_{ob}^* = -R[d \ln k_{ob}/d(1/T)] \quad (12)$$

The corresponding observed preexponential factors, A_{ob} (cm sec^{-1}), were extracted from ΔH_{ob}^* and k_{ob} by using

$$k_{ob} = A_{ob} \exp(-\Delta H_{ob}^*/RT) \quad (13)$$

Calculated activation enthalpies, ΔH_{cal}^* , for comparison with ΔH_{ob}^* can be obtained from estimates of the intrinsic enthalpic barrier ΔH_{int}^* ; this in turn can readily be obtained from ΔG_{int}^* and the intrinsic entropic barrier, ΔS_{int}^* , by using

$$\Delta H_{int}^* = \Delta G_{int}^* + T\Delta S_{int}^* \quad (14)$$

As above, we will neglect the inner-shell component and thereby assume that ΔG_{int}^* equals the values of ΔG_{os}^* obtained from Eq. (5) (Table II). Conventionally, ΔS_{int}^* is estimated by assuming that the inner-shell component is zero, and that the outer-shell component, ΔS_{os}^* , is given by the dielectric continuum model.^{1d} We employ here a modified treatment which yields for electrochemical exchange reactions:^{19,54}

$$\Delta S_{int}^* = \frac{e^2}{8} \left(\frac{1}{a} - \frac{1}{K_p} \right) \left[\frac{1}{\epsilon_{op}^2} \left(\frac{d\epsilon_{op}}{dT} \right) \right] + (\Delta S_{rc}^* - K_1) / (8a + 4) \quad (15)$$

where n is the charge number of the reduced form of the redox couple (zero for the present system), ΔS_{rc}^* is the reaction entropy¹² and K_1 is a constant that depends upon the electron-accepting properties of the solvent. Inserting typical values of ΔS_{rc}^* along with literature values of ϵ_{op} and estimates of K_1 into Eq. (15) yields the estimates of ΔS_{int}^* in each solvent given in Table II (see footnotes for details; these are essentially the same for each redox couple in a given solvent). The resulting estimates of ΔS_{int}^* are small, the "optical" component being largely cancelled by the "static" (reaction entropy) component. Therefore from Eq. (14), $\Delta H_{int}^* = \Delta G_{int}^*$.

In order to obtain calculated activation enthalpies, ΔH_{cal}^* , the temperature dependence of the preexponential factor must also be taken into account. Although K_p and κ_{el} [Eq. (6)] are probably temperature independent, according to Eqs. (9) and (11) v_{os} (and hence v_n) are temperature dependent since τ_L generally decreases with increasing temperature. From the form of Eq. (9), we can write

$$\Delta H_{cal}^* = \Delta H_{int}^* - \Delta H_{\tau}^* \quad (16)$$

where $\Delta H_{\tau}^* = -R(d\ln\tau_L^{-1}/dT^{-1})$. Although the required temperature-dependent dielectric loss data are incomplete for the present solvents, ΔH_{τ}^* varies from zero to 3 kcal mol⁻¹ (Table II: note the values in parentheses are estimated).

The resulting values of ΔH_{cal}^* obtained in this manner from Eq. (16) are listed in Table IV for comparison with the corresponding experimental quantities, ΔH_{ob}^* . Also given in Table IV are calculated preexponential factors, A_{cal} , obtained from the corresponding values of k_{cal} (Eq 11) and ΔH_{cal}^* [cf. Eq. (13)], for comparison with the measured values, A_{ob} . Bearing in mind the uncertainties in the values of ΔH_{ob}^* (± 0.3 to 0.5 kcal mol⁻¹) and those in A_{ob} (ca. 2-5 fold), the agreement between the calculated and observed activation parameters is

satisfactory. The best agreement is seen for $\text{Cr}(\text{C}_6\text{H}_5)_2^{+/\circ}$; for the two metallocene couples, typically $\Delta H_{ob}^* < \Delta H_{calc}^*$ and $A_{ob} < A_{calc}$, although the discrepancies are not large.

DISCUSSION

Electrochemical Exchange Kinetics

Although all three sets of calculated rate constants given in Table III are mostly within tenfold of the observed parameters, it is clear that that inclusion of a preexponential factor accounting for the dynamics of solvent reorganization yields a substantially improved description of the solvent-dependent kinetics. This in itself is notable since it suggests that the molecular solvent properties can play an important role in the kinetics of outer-sphere electron transfer beyond influencing the barrier height. We have briefly discussed this matter in a preliminary communication.⁶

It is of interest to reconcile these findings with the anticipated applicability of the alternative frequency factor relations Eqs. (7), (9), (10), and (11). As noted above, Eqs. (7) and (10) are TST expressions, whereas Eqs. (9) and (11) are not. A key issue is the extent to which inner- rather than outer-shell motion controls the preexponential factor. All the present reactions have only small inner-shell barriers. Nevertheless, with the exception of $\text{Mn}(\text{Cp}')_2^{+/\circ}$ the values of ΔG_{is}^* are sufficiently large ($0.15 - 0.25 \text{ kcal mol}^{-1}$) so that according to Eq. (7), v_{is} constitutes the predominant component of v_n , provided that $v_{os} \leq 1 \times 10^{12} \text{ sec}^{-1}$. This latter condition is apparently met since TST estimates of v_{os} in the range ca. 0.5 to $1 \times 10^{12} \text{ sec}^{-1}$ are obtained from Eq. (10), thereby justifying the assumption $v_{is} \gg v_{os}$ employed above to obtain k_{cal} (Eq. 7).

On the other hand, ΔG_{is}^* for $Mn(Cp')_2^{+/\circ}$ is sufficiently small so that Eq. (7) instead predicts that v_n essentially equals v_{os} , yielding 1.5 to 2 fold smaller predicted values of k_{cal} (Eq 7) than for the other couples in spite of the slightly lower free-energy barrier for $Mn(Cp')_2^{+/\circ}$. In contrast, the k_{ob} values for $Mn(Cp')_2^{+/\circ}$ are slightly larger than for the other couples in a given solvent (Table III), as expected given the differences in ΔG_{is}^* if v_n is the same for each reaction. Indeed, the observed reactivity trend for the homologous series $Mn(Cp')_2^{+/\circ} > Fe(Cp')_2^{+/\circ} > Co(Cp')_2^{+/\circ}$ (Table III) in each solvent is quantitatively consistent with the differences in ΔG_{is}^* noted above. This therefore corroborates the above findings indicating a breakdown in the TST model embodied in Eq. (7).

In contrast, these results are intuitively reasonable on the basis of the model embodied in Eq. (9) since in contrast to the TST approach which predicts that the fastest dynamical component of the barrier will tend to dominate v_n ,⁵⁵ such overdamped solvent relaxation is anticipated to dominate v_n when v_{os} is slower than inner-shell motion.

Having exposed a key limitation of Eq. (7), it is nonetheless important to ascertain under what conditions inner-shell motion will dominate v_n even in slowly relaxing solvents ($\tau_L \gtrsim 10^{-12}$ sec). This question has recently been addressed, and the following approximate inequality derived,^{2f} obeyance to which denotes conditions for which $v_{os} \approx v_n$:

$$(\Delta G_{is}^*/\Delta G_{int}^*)^{1/2} v_{is} \exp(-\Delta G_{is}^*/k_B T) \approx \tau_L^{-1} \quad (17)$$

Inserting the typical values of $\Delta G_{int}^* = 5 \text{ kcal mol}^{-1}$, $v_{is} = 6 \times 10^{12} \text{ sec}^{-1}$, $\Delta G_{is}^* = 0.2 \text{ kcal mol}^{-1}$ into Eq. (17) yields a left-hand-side equal to

$8.5 \times 10^{11} \text{ sec}^{-1}$. This suggests that TST will not apply for the present reactions in the "slowly relaxing" solvents formamide, NMF, DMSO, and benzonitrile, for which $\tau_L^{-1} < 8.5 \times 10^{11} \text{ sec}^{-1}$. The other solvents considered here, acetonitrile, acetone, CH_2Cl_2 , and perhaps DMF appear to be "borderline cases" not only with respect to the possible influence of inner-shell motion upon v_n , but also with regard to solvent inertial effects since the τ_L values are sufficiently small ($\leq 1 \times 10^{-12} \text{ sec}$) so that Eqs. (9) and (11) yield significantly different estimates of v_{os} .

Nonetheless, the simple overdamped solvent model embodied in [Eq. (9)] yields estimates of k_{cal} that best mimic the solvent-dependent values of k_{ob} (Table III). In tentatively accepting Eq. (9) as providing the most apt description of the reaction dynamics, it is worth noting that at least the absolute estimates, if not the solvent-dependence, of k_{cal} contain several uncertainties. Not the least of these is the possibility that the dielectric continuum model [Eq. (5)] may incorrectly estimate the outer-shell barrier.

We have recently outlined a phenomenological approach⁵⁶ that indicates that this model may significantly underestimate ΔG_{os}^* , although the opposite conclusion has been deduced for certain conditions.⁵⁷ However, strong evidence favoring the applicability of the dielectric continuum model for estimating ΔG_{os}^* for $\text{Fe}(\text{Cp})_2^{+/\circ}$ is obtained from its success in rationalizing the solvent-dependence of optically induced electron transfer in binuclear ferrocene complexes,^{58,59} including several solvents (acetone, acetonitrile, benzonitrile) employed here for which v_{os} varies greatly (Table II). A key difference between optical and thermal electron transfer is that only the barrier height, rather than the solvent dynamics, influences the former process. Slightly (0.5 - 1 kcal mol⁻¹) smaller values of ΔG_{os}^* are deduced from Eq. (5) if the electrode imaging term ($1/R_e$) is included,

using reasonable estimates of the reactant-electrode distances.³⁰ Nevertheless, the calculated enthalpic barriers are close (mostly within 1 kcal mol⁻¹) to the observed values, especially for Cr(C₆H₅)₂^{+/0} (Table IV), indicating that Eq. (5) is at least approximately applicable to the present systems. This is not too surprising since the reactant's small charge and nonpolar ligands should facilitate the applicability of dielectric continuum treatments.^{20,56}

Comparison with Homogeneous Self-Exchange Kinetics

Given that the foregoing indicates the importance of solvent relaxation dynamics to electrochemical reactions involving chiefly outer-shell reorganization, it is of interest to ascertain if similar effects can be discerned for related homogeneous exchange processes. Of particular significance are the solvent-dependent bimolecular rate parameters for Fe(O_p)₂^{+/0} reported by Wahl and coworkers.^{5a} Table V contains a summary of their data, including values of ΔH_{ob}^* (kcal mol⁻¹) and A_{ob} (M⁻¹ sec⁻¹)⁶⁰ as well as k_{ob} (M⁻¹ sec⁻¹) in eight solvents, four of which were employed for the electrochemical studies (Table III). Alongside these experimental values are summarized the corresponding calculated quantities k_{cal} , ΔH_{cal}^* , and A_{cal} . These were obtained using essentially the same procedures to those described above, with the following modifications. A homogeneous precursor formation constant, K_p^h (M⁻¹ sec⁻¹), was employed in Eq. (6), estimated from the analogous relation^{33,38,39}

$$K_p^h = 4\pi N r^2 \delta r_h \quad (18)$$

where N is Avogadro's number, r is the internuclear reactant separation in the transition state (taken as 2a = 7.6 Å), and δr_h is the "reaction zone thickness", taken again as 0.6 Å.^{33,42} The value of ΔG_{18}^* (0.3 kcal mol⁻¹) is twice the electrochemical value (Table II); the outer-shell barriers are obtained from [cf Eq. (5)]:³⁴

$$\Delta G_{os}^* = \frac{e^2}{4} \left(\frac{1}{a} - \frac{1}{R_h} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (19)$$

where R_h is the internuclear distance, again taken as 2a. (Note that these estimates of ΔG_{os}^* are numerically equal to the above values for electrochemical exchange.) The entropic barriers, ΔS_{int}^* , were also set equal to zero, in view of the small electrochemical estimates given in Table II and the incompleteness of the required ΔS_{rc}^* data.

If it is assumed, as is conventional, that the preexponential factor is solvent independent, from Eqs. (2) and (19) we can express k_{ob} as^{5b}

$$\ln k_{ob} = K - \frac{e^2}{4RT} \left(\frac{1}{a} - \frac{1}{R_h} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (20)$$

where K is a constant which contains both A and ΔG_{is}^* . Wahl et al noted that whereas Eq. (20) predicts a ca. 20 fold variation in k_{ob} for the solvents listed in Table V (for $a = 0.5$ $R_h = 3.8 \text{ \AA}$), the experimental values of k_{ob} are mostly within ca. twofold of each other.^{5a} A possible cause of these discrepancies is errors in estimating ΔG_{os}^* due to uncertainties in the transition-state geometry as well as in the simple "two-sphere" variant of the continuum model embodied in Eqs. (19) and (20)^{1f}. These factors cannot account, however, for the observed qualitative inability of Eq. (20) to describe the variations of k_{ob} upon solvent substitution,^{5a} especially given the aforementioned applicability of the continuum model to optical electron transfer within biferrrocenes.^{5g} The values of k_{cal} given in Table V were obtained instead using the solvent-dependent frequency factors estimated from Eq. (9). Comparison between the corresponding values of k_{cal} and k_{ob} shows that although generally $k_{cal} > k_{ob}$ the former successfully mimics the relative solvent-independence of the latter. Thus in most solvents $k_{cal} = (15 \text{ to } 20) k_{ob}$; the only exceptions to this are methanol and CH_2Cl_2 .

This surprisingly mild calculated solvent dependence follows from a broad tendency of solvents having larger values of ϵ_{sp} and hence smaller ΔG_{os}^* to also exhibit longer relaxation times and hence smaller effective values of v_{os} . The variations in the preexponential and exponential components of k_{cal} thereby tend to cancel.

The ca. 20-fold discrepancies between k_{cal} and k_{ob} may be due in part to systematic errors in calculating the absolute values of ΔG_{os}^* and/or A. If a particular geometry (such as the parallel juxtaposition of a pair of aromatic ligand rings) is preferred in order to provide effective orbital overlap, then K_p^h and hence A can be substantially smaller than predicted from Eq. (18).^{5b} Judging by the much better agreement between k_{ob} and k_{cal} (Eq 9) for the electrochemical reactions (Table III), such steric effects are presumably less important in the heterogeneous reaction environment.

Further evidence suggesting the presence of complicating factors for such homogeneous self-exchange processes is obtained from the ca. 40 fold larger value of k_{ob} for the self-exchange of $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/\circ}$ ($6 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ ^{5b}) relative to that for $\text{Fe}(\text{Cp})_2^{+/\circ}$ ($1.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ ^{5a}) in DMSO, even though very similar values are predicted from theoretical considerations and are indeed observed in the heterogeneous environment (Table III). Again in contrast to the electrochemical systems (Table IV) the ΔH_{ob}^* values for $\text{Fe}(\text{Cp})_2^{+/\circ}$ self exchange are substantially ($2-4 \text{ kcal mol}^{-1}$) smaller than ΔH_{cal}^* . Even larger discrepancies are seen between A_{ob} and A_{cal} ; typically $A_{\text{ob}} \sim (10^{-3} \text{ to } 10^{-5})A_{\text{cal}}$. It seems clear that the energetics of the biomolecular reactions contain subtleties, perhaps associated with the approach of the reactant pair, that are absent for the electrochemical exchange reactions.

Implications for Other Systems

The self-exchange kinetics of several other systems besides $\text{Fe}(\text{Cp})_2^{+/\circ}$ have been studied as a function of the solvent,^{3,62} although few reports have included a systematic variation in dielectric solvent properties. One objective has been to examine the ability of the dielectric continuum model as embodied in Eq. (20) to predict the dependence of k_{ob} upon the solvent.

Interestingly, while the solvent dependence of k_{ob} for some systems, such as benzonitrile^{3c} as well as $\text{Fe}(\text{Cp})_2^{+/\circ}$ discussed above, show qualitative deviations from Eq. (20), a few others exhibit tolerable agreement.⁶² Examples of the latter behavior are tris-hexafluoroacetylacetone/ruthenium(III)/(II) and related couples ["Ru(hfac)(III)/(II)"],⁶³ and molecule-cation couples involving ρ -phenylenediamine derivatives.^{3e}

These behavioral differences can be rationalized in terms of the present theoretical treatment if inner-shell motion rather than solvent relaxation provides the predominant contribution to the barrier crossing rate, so that v_n is approximately solvent independent. According to Eq. (17), this condition will occur for common polar solvents, for which usually $\tau_L \leq 2 \times 10^{-12}$ sec, when $\Delta G_{\text{is}}^* \geq 1$ to $1.5 \text{ kcal mol}^{-1}$, (taking the typical values of $\Delta G_{\text{os}}^* = 5 \text{ kcal mol}^{-1}$ and $v_{\text{is}} = 1 \times 10^{13} \text{ sec}^{-1}$). Although the structural data required to calculate ΔG_{is}^* are lacking, this circumstance is likely for Ru(hfac)(III)/(II) given that significant bond-distance changes are both anticipated and observed for other Ru(III)/(II) couples involving oxygen-donor ligands.⁶⁴ Values of ΔG_{is}^* around $0.5 \text{ kcal mol}^{-1}$ have been estimated empirically for the ρ -phenylenediamine couples;^{3e} somewhat larger values, ca. 1 kcal mol^{-1} , are obtained from bond-length data.⁶⁵ The observed agreement of the solvent-dependent k_{ob} values for these systems with the functional form of Eq. (20)^{3a} is therefore tentatively

ascribed to the prominent contribution of inner-shell vibrations to v_n . An apparent obeyance to Eq. (20), or at least its functional form, can occur even when $v_n \approx v_{os}$ if solvents are employed that display comparable values of v_{os} or where the solvent dependence of v_{os} is functionally similar to that of $\exp(-\Delta G_{os}^*/RT)$. For example, the former circumstance may account for the approximate success of Eq. (20) for bis-biphenylchromium(I)/(0) self exchange,^{5b} since the values of v_{os} do not differ greatly in the pure solvents employed in that study.⁶⁶ A more detailed analysis of these and other systems will be given elsewhere.

Irrespective of the details, it is clear that the extent to which the measured kinetics are influenced by solvent relaxation dynamics is sensitive to the nature and extent of the inner-shell barrier as well as to v_{os} . Inner-shell barriers around ca. 0.2 to 2 kcal mol⁻¹, associated with the small structural changes that almost inevitably accompany electron transfer, are commonly anticipated even for reactions where solvent reorganization dominates the free-energy barrier. The numerical value of the preexponential factor can therefore be very sensitive to the electronic structure of the redox couple. Unfortunately, the structural data required to estimate ΔG_{is}^* are often lacking, especially for organic systems.

These considerations are quite apart from the influence upon A_{ob} associated with the possible occurrence of nonadiabatic pathways (i.e., $\kappa_{el} < 1$). In the context of the present discussion, it should be borne in mind that the expression for v_{os} [Eq. (11)] is itself dependent on the reaction adiabaticity.^{2a} (*vide supra*) Even though Eq. (11) is appropriate for reaction channels that approach adiabatic ($\kappa_{el} \sim 1$), another relation is appropriate for reactions featuring stronger electronic coupling ("case A" rather than "case B" in ref. 2a).

The overall message is that the solvent sensitivity, as well as the absolute values, of the preexponential factor for electron-transfer reactions that feature chiefly outer-shell reorganization appear to be strongly dependent on a number of parameters, most prominently τ_L , τ_{rot} , v_{is} , k_{el} , and ΔG^*_{is} . Although hitherto neglected, it is apparent that the first as well as the last three parameters can provide an important influence upon electron-transfer reactivity. A unified theoretical treatment combining each of these various elements is yet to appear. In the meantime, it is hoped that the present work will provide a stimulus for further detailed examinations of solvent-dependent reactivities, both in homogeneous solution and at electrode surfaces.

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60. Note that the values of ΔH^*_{ob} in Table V equal the quantities labeled " E_{act}^{ob} " in ref. 5a., even though somewhat different "activation enthalpies" were quoted (Table V of ref. 5a.). These latter quantities were corrected for the anticipated temperature dependence of the collision frequency. This correction is not applied here since it is inappropriate when using the encounter preequilibrium treatment.
61. The discrepancies between k_{ob} and $k_{ob}^{+/-}$ are smaller for $\text{Fe}(\text{Cp}')_2^{+/-}$ than noted in Table V for $\text{Fe}(\text{Cp})_2^{+/-}$, at least in acetonitrile, since $k_{ob}^{+/-}$ for the former is eightfold larger than for the latter. Methyl substitution, however, has only a more modest effect upon the electrochemical exchange rates for cobalticinium-cobaltocene (Table III).

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TABLE I Relevant Properties of Metallocene and Metal Arene Redox Couples

Redox Couple ^a	Solvent ^b	E_f	c	ΔS°_{rc}	d	D	e	Δa	h	ν_{1s}	ν_{1s}	ΔG_{1s}^n
		mV vs sce		cal deg ⁻¹ mol ⁻¹		cm ² sec ⁻¹				sec ⁻¹	sec ⁻¹	kcal mol ⁻¹
$Fe(Cp')_2^{+/0}$	Acetonitrile	-80		~11				1.3x10 ⁻⁵	f	-0.035	6.4x10 ¹²	0.15
	Acetone	-15		14				1.5x10 ⁻⁵	f			
	CH_2Cl_2	-130		5				1.3x10 ⁻⁵	f			
	NMF	-75		3				1.4x10 ⁻⁶	f			
	DMF	60		12				7.7x10 ⁻⁶	f			
	DMSO	-40		8.5				3.2x10 ⁻⁶	f			
										9.10 ¹²	k	~0.15
$Fe(Cp)_2^{+/0}$	Acetonitrile	425		11.5								
	Acetonitrile	-1510						1.3x10 ⁻⁵	g	0.045	6x10 ¹²	1
	DMF	-1395						8x10 ⁻⁶	g			0.22
$Co(Cp)_2^{+/0}$	Acetonitrile	-905		17				1.8x10 ⁻⁵	g			~0.25
	DMF	-830		16				7x10 ⁻⁶	g			
	Formamide	-1045		4.5				4.8x10 ⁻⁶	g			
										9x10 ¹²	1	
$Mn(Cp')_2^{+/0}$	Acetonitrile	-540						1.5x10 ⁻⁵	f	-0.014	6x10 ¹²	1
	DMF	-490						7.5x10 ⁻⁶	f			0.025
$Cr(C_6H_6)_2^{+/0}$	Acetonitrile	-770		16				1.3x10 ⁻⁵	g	~0.045	8.5x10 ¹²	~0.2
	DMF	-710		16.5				8x10 ⁻⁶	g			
	Formamide	-930		2				5x10 ⁻⁶	g			
	Benzonitrile	-795		5				2.4x10 ⁻⁶	g			

Footnotes to Table I

a Cp = cyclopentadiene, Cp' = pentamethylcyclopentadiene

b NMR = N-methylformamide, DMF = N,N-dimethylformamide, DMSO = dimethylsulfoxide

c Formal potential of redox couple, obtained by using a:c. polarography or cyclic voltammetry in indicated solvent containing 0.1 M tetrabutylammonium hexafluorophosphate. Potentials measured against aqueous saturated calomel electrode in contact with nonaqueous electrolyte.

d Reaction entropy of redox couple,¹¹ obtained from temperature dependence of E_f using nonisothermal cell arrangement as detailed in ref. 12.

e Diffusion coefficient for either oxidized or reduced form of redox couple as indicated, determined from d.c. polarography.

f For reduced form.

g For oxidized form.

h Change in metal-ring bond distance between oxidized and reduced forms of redox couple. Obtained from corresponding metal-carbon bond distances, Δr_{pd} and Δr_{pd^+} , determined from X-ray crystallography, as follows: $\text{Fe}(Cp')_2^{+/0}$; $\Delta r_{\text{pd}} = 2.097, \Delta r_{\text{pd}^+} = 2.050; \text{Fe}(Cp')_2^{0/+}$; $\Delta r_{\text{pd}} = 2.049, \Delta r_{\text{pd}^+} = 2.105; \text{Fe}(Cp)_2^{+/0}$; $\Delta r_{\text{pd}} = 2.096, \Delta r_{\text{pd}^+} = 2.130; \text{Fe}(Cp')_2^{0/+}$; $\Delta r_{\text{pd}} = 2.112, \Delta r_{\text{pd}^+} = 2.176; \text{Fe}(C_6H_5)_2^{+/0}$; $\Delta r_{\text{pd}} = 2.08, \Delta r_{\text{pd}^+} = 2.029, \Delta r_{\text{pd}} = 2.13, \Delta r_{\text{pd}^+} = 2.19$.

i Average frequency of inner-shell (metal-ring) vibration (sec^{-1}) for oxidized and reduced forms of redox couple, from corresponding totally-symmetrical Raman frequency, ν_R (cm^{-1}), measured or estimated as noted.

j Estimated from corresponding value of ν_R for $\text{Fe}(Cp)_2^{+/0}$ (300 cm^{-1} 13s) by accounting for additional mass of methyl groups assuming an identical force constant.

k From experimental value of ν_R ($\approx 300 \text{ cm}^{-1}$ 13s).

l Estimated from value for $\text{Fe}(Cp')_2^{+/0}$ or $\text{Fe}(Cp)_2^{+/0}$, by noting relation between ν_R and metal-carbon bond distance. 13s

m From experimental value of ν_R ($\approx 275 \text{ cm}^{-1}$ 16s).

n Inner-shell electrochemical barrier, from values of Δs and ν_{18} using Eqs. (3) and (4). Values estimated to be accurate at least $\pm 20\%$, except for $\text{Co}(Cp)_2^{+/0}$ and $\text{Cr}(C_6H_5)_2^{+/0}$, ca $\pm 30\text{-}50\%$.

TABLE II Solvent and Related Properties at 25°C

Solvent	ϵ_{op}^a	ϵ_b^b	ΔG_{os}^c kcal mol ⁻¹	ΔS_{int}^d deg ⁻¹ mol ⁻¹	τ_D^e 10 ⁻¹² sec	τ_L^e 10 ⁻¹² sec	v_{op}^f (Eq. 9) ¹ 10 ¹² sec ⁻¹	v_{os}^g (Eq. 11) ¹ 10 ¹² sec ⁻¹	ΔH_f^h ° kcal mol ⁻¹
Acetonitrile	1.80	37.5	5.75	-1.5	3.3 ^f	~0.2	4.5	1.3	1.1
Acetone	1.84	20.7	5.4	-1.0	3.3 ^g	0.3	3.0	0.8	1.0
CH ₂ Cl ₂	2.03	9.0	4.2	~4	1.5 ^h	~0.4	1.9	0.55	(~1)
Formamide	2.09	110	5.1	1.5	37 ⁱ	2.4	0.35	0.35	~3.0
MF	2.04	182	5.25	-0.5	123 ^j	3.6	0.24	0.22	~2.5
MF	2.04	36.7	5.05	-0.5	11.0 ⁱ	1.3	0.65	0.3	~1.0
DMSO	2.18	46.7	4.7	-1.5	19.6 ⁱ	2.3	0.34	0.3	(~1.5)
Acenonitrile	2.33	25.2	4.2	~1	38 ^j	5.7	0.13	0.13	(~1.5)

Footnotes

Optical dielectric constant, from refractive index data given in ref. 17.

Static (i.e. zero frequency) dielectric constant, from refs. 17 and 18.

Outer-shell intrinsic free energy of activation in given solvent, from Eq. (5) with $a = 3.8 \text{ \AA}$ and $R = \infty$ (see text), using listed values of ϵ_{op} and ϵ_b .

Intrinsic entropy of activation in given solvent, from Eq. (15) with $a = 3.8 \text{ \AA}$ and $R = \infty$ (see text). Values of ϵ_{op}^j ($d\epsilon_{op}/dR$) taken from ref. 17. Values of ΔS^o as follows: acetonitrile, 13 cal deg⁻¹ mol; acetone, 15; CH₂Cl₂, 5.9^p; formamide, 3; NMP, 4; DMF, 14; DMSO, 10; benzocyanide, ~10. Values of K_1 taken as zero except in formamide ($2 \text{ cal deg}^{-1} \text{ mol}^{-1}$), and NMR (~5) (see text and refs. 19 and 20 for details).

Debye relaxation time, obtained from dielectric loss measurements in references cited.

Footnotes to Table II Continued

^hRef. 23.

ⁱRef. 24.

^jRef. 25.

^kLongitudinal solvent relaxation time, determined from corresponding values of τ_D with values of ϵ_∞ and ϵ_s given in references cited for τ_D , by using Eq. (8).

^lSolvent preexponential factor, obtained from values of τ_L and ΔG^\ddagger by using Eq. (9).

^mSolvent preexponential factor, obtained from Eq. (11) using listed values of τ_L , ϵ , and ΔG^\ddagger , and estimates of τ and τ_C , evaluated from Eqs. (10a) and (10b), respectively. These estimates of τ^{rgt} and τ^{rot} , respectively, for each solvent are as follows: acetonitrile, 0.45 psec; acetone, 0.97 psec; 1.9; CH_2Cl_2 , 0.2 psec; 0.4; formamide, 0.5 psec; 5.7; NMR, 0.65 psec; DMF, 0.85 psec; DMSO, 0.6 psec; 24.3; benzonitrile, 1.0 psec, 3.2.

ⁿEnthalpy of activation associated with longitudinal solvent relaxation; determined from $\Delta H^\ddagger = -R \left(\frac{d \ln \tau_L}{dT} \right)^{-1}$, where τ_L is evaluated from Eq. (8). Values obtained from temperature-dependent dielectric loss data using literature sources listed in τ_D column. Values in parenthesis are estimated.

TABLE III Comparison between Experimental and Calculated Rate Constants (cm sec^{-1}) for Electrochemical Exchange
at 23°C

Solvent	Calculated Rate Constants, k_{cal}			Observed Rate Constants, k_{ob} ^d			
	(Eq. 7) ^a	(Eq. 9) ^b	(Eq. 11) ^c	$\text{Mn}(\text{Cp}')_2^{+/\ominus}$	$\text{Fe}(\text{Cp}')_2^{+/\ominus}$	$\text{Co}(\text{Cp}')_2^{+/\ominus}$	$\text{Cr}(\text{C}_6\text{H}_6)_2^{+/\ominus}$
Acetonitrile	0.30	1.6	0.5	~ 4	e	~ 3.5	3.0
Acetone	0.55	2.0	0.5	~ 4	~ 3.5	~ 3	2.5
CH_2Cl_2	4.0	10	2.8	f	~ 2	0.55	0.55
Formamide	0.9	0.4	0.35	f	0.9	0.8	0.6
NMP	0.7	0.20	0.2	f	~ 2	~ 1.5	0.6
DMP	1.0	0.6	0.35	0.9	0.85	0.75	0.55
DMSO	2.5	0.7	0.65	0.4	0.4	0.25	0.3
Benzonitrile	4.2	0.65	0.6				

Footnotes

^a Rate constant (cm sec^{-1}) calculated from Eqs. (2), (5), and (6) with $\Delta G_{12}^{\text{st}} = 0$, $\Delta G_{08}^{\text{st}}$ as given in Table II, K_{12}^{KCl} = 0.6 A_{n} , v_n obtained from Eq. (7), with $\Delta G_{12}^{\text{st}} = 0.2$ kcal mol $^{-1}$, $v_{12} = 6 \times 10^{12} \text{ sec}^{-1}$, and $v_{08} \ll v_{12}$ (see text).

^b As footnote a, but with v_n set equal to v_{08} obtained from Eq. (9) (Table II).

^c As footnote a, but with v_n set equal to v_{08} obtained from Eq. (11) (Table II).

^d Observed rate constant (cm sec^{-1}) obtained for stated redox couple in solvent indicated, containing 0.1 M TBAP. Values reproducible to ca. $\pm 20\%$.

^e Measurement precluded due to spurious a.c. polarographic behavior.

^f Measurement precluded due to insufficient solubility of metallocene.

TABLE IV Comparison between Experimental and Calculated Activation Parameters for Electrochemical Exchange

Solvent	ΔH^* _{cal} ^a	A_{cal} ^b	ΔH^* _{ob} ^c	A_{ob} ^d	ΔH^* _{ob} ^c	A_{ob} ^d	ΔH^* _{ob} ^c	A_{ob} ^d
		$Fe(CP')_2^{+}/o$		$Co(CP)_2^{+}/o$		$Cr(C_6H_6)_2^{+}/o$		
Acetonitrile	6.5	9×10^4			4.5	6×10^3	6.2	1×10^5
Acetone	6.1	6×10^4	4.5	8×10^3	5.0	1×10^4	7.5	5×10^5
Formamide	≈ 8.5	$\sim 5 \times 10^5$			6.2	2×10^4	7.5	1.5×10^5
NMF	7.5	6×10^4					6.0	2×10^4
DMF	5.8	1.0×10^4	4.5	5×10^3	5.0	$\sim 8 \times 10^3$	5.5	1.5×10^4
DMSO	≈ 6	$\sim 2 \times 10^4$	5.2	6×10^3	5.5	8×10^3	5.8	8×10^3
Benzonitrile	≈ 6	$\sim 2 \times 10^4$					5.5	4×10^3

Footnotes

^aCalculated enthalpy of activation (kcal mol⁻¹), obtained from Eqs. (14) and (16), with ΔS^*_{int} and ΔH^* from Table II, and ΔG^*_{int} assumed equal to ΔG^*_{ob} , from Table III.

^bCalculated preexponential factor (cm sec⁻¹), obtained from ΔH^* _{cal} and k_{cal} (Eq. 11) (Table III) using $A_{cal} = k_{cal} \exp(\Delta H^*/RT)$.

^cExperimental enthalpy of activation (kcal mol⁻¹) for given redox couple, obtained from temperature derivative of k_{ob} by using Eq. (12). Uncertainties in listed values typically 0.3 - 0.5 kcal mol⁻¹.

^dExperimental preexponential factor (cm sec⁻¹) for given redox couple, obtained from values of ΔH^* _{ob} and k_{ob} (Table III). Uncertainties in listed values typically 2-5 fold.

TABLE V Comparison between Experimental and Calculated Rate Parameters for Ferricinium-Ferroocene Self Exchange

Solvent	ΔG^{\ddagger}_{cs} ^a kcal mol ⁻¹	v_{os} ^b 10^{12} sec ⁻¹	k_{cal}^* M ⁻¹ sec ⁻¹	$\Delta H^{\ddagger}_{cal}$ kcal mol ⁻¹	A_{cal} ^c M ⁻¹ sec ⁻¹	k_{ob}^* M ⁻¹ sec ⁻¹		k_{ob} kcal mol ⁻¹	ΔH^{\ddagger}_{ob} M ⁻¹ sec ⁻¹	A_{ob}^* M ⁻¹ sec ⁻¹
						k_{ob} M ⁻¹ sec ⁻¹	ΔH^{\ddagger}_{ob} kcal mol ⁻¹			
Methanol	5.85	0.12 ^c	1.5×10^6	.99	$\sim 5 \times 10^{12}$	6.0×10^6	3.0×10^9			
Acetonitrile	5.75	4.5	7×10^7	7.2	1.5×10^{13}	5.3×10^6	2.5×10^{10}			
Nitromethane	5.4	3.5 ^d	1.0×10^8	6.5	6×10^{12}	5.8×10^6	4.0×10^9			
Acetone	5.4	3.0	8.5×10^7	6.7	7×10^{12}	4.6×10^6	4.8×10^{10}			
DMSO	4.7	0.34	3.2×10^7	.96.5	$\sim 2 \times 10^{12}$	1.6×10^6				
Nitrobenzene	4.2	0.35 ^e	7.7×10^7	.96	$\sim 2 \times 10^{12}$	2.3×10^6	2.3×10^8			
CH_2Cl_2	4.2	1.9	4.1×10^8	.96	$\sim 1 \times 10^{13}$	4.3×10^6	2.0×10^8			
$(\text{CH}_2\text{Cl})_2$	4.15	0.45 ^f	1.1×10^8	6.0	3×10^{12}	4.3×10^6	2.0×10^8			

Footnotes

^aOuter-shell free energy of activation, determined from Eq. (19) with $a = 3.8 \text{ \AA}$, $R_h = 2\text{a}$, using values of ϵ_{op} and ϵ_s taken from refs. 17, 18.

^bSolvent preexponential factor, obtained from Eq. (9) using values of τ_L noted in Table II, determined from τ_D , ϵ_s , ϵ_{∞} [Eq. (8)] from source noted.

^cRef. 26.

^dRef. 27.

^eRef. 25.

^fRef. 28.

^gRate constant calculated from Eqs. (2) and (6) with $K_h^h = 0.262 \text{ M}^{-1}$ [from $K_h^h = 4\pi N r^2 \delta r$, with $r = 7.6 \text{ \AA}$ (1.e-2a), and $\delta r = 6 \times 10^{-9} \text{ cm}$ (see text)], and using listed values of ΔG^{\ddagger}_{os} and ν_{os} . With $\Delta G^{\ddagger}_{int} = \Delta G^{\ddagger}_{os} + 0.3 \text{ kcal mol}^{-1}$.

Footnotes to Table V Continued

^hCalculated enthalpy of activation, obtained from $\Delta H^*_{cal} = \Delta U^* + \Delta G^*_{1S} + \Delta H^*_{T,S}$, with $\Delta G^*_{1S} = 0.3$ kcal mol⁻¹, $\Delta S^* = 0$, and ΔH^* determined or estimated^g from temperature dependence of v_{OS}^{1S} (see Table II and references cited for v_{OS}^{1S}).

ⁱCalculated preexponential factor, obtained from corresponding values of k_{cal} and ΔH^*_{cal} .

^jObserved rate constant for homogeneous $Fe(Cp)_2$ self exchange at 25°C, from ref. 4.

^kObserved enthalpy of activation, equal to Arrhenius activation energy, from ref. 4.

^lObserved preexponential factor, obtained from corresponding values of k_{ob} and ΔH^*_{ob} .